

PATENT ABSTRACTS OF JAPAN

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(54) MODIFIED WATER-ABSORPTIVE RESIN PARTICLE AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject particles improved in rupture stress and reduced in brittleness, thus useful for paper diapers, by surface-crosslinking water-absorptive resin particles comprising acrylic acid etc., as the main constitutive unit under heating, and then adjusting the water content of the resin particles within a specified range by addition of water.

SOLUTION: The objective water-absorptive resin particles are obtained by surface-crosslinking under heating (A) water-absorptive resin particles comprising acrylic acid (salt) as the main constitutive unit by using (B) a crosslinking agent having two or more functional groups reactive with the acrylic acid (salt), and then adjusting the water content of the resin particles to 3-9wt.% by addition of water.

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A. Relevance of the Above-identified Document

The following is an English translation of non-English language information that may be relevant to the issue of patentability of the claims of the present application.

B. Translation of the Document

1. TITLE OF THE INVENTION

**REFORMED WATER ABSORBENT RESIN PARTICLES
AND PRODUCTION METHOD THEREOF**

2. ABSTRACT

[OBJECT]

To obtain water absorbent resin particles whose breakability (fracture stress) and fragility of the particles at a time when mechanical shear stress is applied are improved.

[MEANS TO SOLVE THE PROBLEMS]

Water is added to water absorbent resin particles whose main composition is acrylic acid and/or acrylic acid salt and whose surface and vicinity thereof are cross-linked with heating by a cross-linking agent having more than two functional groups capable of reacting with the acrylic acid and/or the acrylic acid salt so that water content ranges from 3 through 9%, the addition being

performed after the cross-linking. As a result, fracture stress of the particles become not less than 30N/m².

3. CLAIMS

1. A method for producing water absorbent resin particles whose fragility is reformed,

said method comprising the step of

adding water to water absorbent resin particles whose main composition is acrylic acid and/or acrylic acid salt and whose surface and vicinity thereof are cross-linked with heating by a cross-linking agent having more than two functional groups capable of reacting with the acrylic acid and/or the acrylic acid salt so that water content ranges from 3 through 9%,

said step being performed after the cross-linking.

2. The method as set forth in claim 1, wherein an amount of water to be added ranges 2 through 15 wt% relative to a weight of the water absorbent resin particles.

3. The method as set forth in claim 1 or 2, wherein inorganic salt and/or inorganic hydroxide is included in the water to be added.

4. The method as set forth in claim 3, wherein the inorganic salt is at least one selected from alkaline metal

salt, alkaline earth metal salt, and aluminum salt.

5. The method as set forth in claim 3 or 4, wherein density of the inorganic salt relative to the water ranges from 5 through 50 wt%.

6. The method as set forth in claims 1 through 5, wherein addition of the water to the water absorbent resin particles is performed in a stirring mixer having a stirring rotor.

7. The method as set forth in claims 1 through 6, wherein fraction stress of the reformed water absorbent resin particles is not less than 30N/m^2 .

8. Water absorbent resin particles whose fragility is reformed so that fracture stress of the particles is not less than 30N/m^2 ,

said water absorbent resin particles being obtained by adding water to absorbent resin particles whose main composition is acrylic acid and/or acrylic acid salt and whose surface and vicinity thereof are cross-linked with heating by a cross-linking agent having more than two functional groups capable of reacting with the acrylic acid and/or the acrylic acid salt so that water content ranges from 3 through 9%.

4. DETAILED DESCRIPTION OF THE INVENTION

[FIELD OF THE INVENTION]

The present invention relates to reformed water absorbent resin particles and a production method thereof. More particularly, the present invention relates to water absorbent resin particles whose breakability (fracture stress) and fragility at a time when mechanical power is applied are reformed by adding water to water absorbent resin particles whose surfaces have been cross-linked with heating so that water content is within a specific range.

[PRIOR ART]

It is general to use a water absorbing resin in a sanitary material such as a sanitary napkin, a disposable diaper, or the like. Examples of such water absorbent resin include a substantially water-insoluble cross-linked polymer such as cross-linked polyacrylic acid salt, self-cross-linked polyacrylic acid salt, cross-linked starch-acrylic acid salt graft copolymer, or the like. Recently, there has appeared a so-called surface-cross-linked water absorbent resin in which surface and vicinity thereof of water absorbent resin particles is cross-linked with heating by a cross-linking agent including not less than two functional groups capable of reacting with acrylic acid and/or acrylic acid salt, so as to improve absorbent characteristics and gel

properties of these water absorbent resins.

[PROBLEMS TO BE SOLVED]

Although the surface-cross-linked water absorbent resin obtained through cross-linking with heating has higher absorbent characteristics and gel properties than a conventional water absorbent resin obtained through surface-cross-linking with non-heating, resin particles of the surface-cross-linked water absorbent resin become hard and fragile because cross-linking density at surfaces and vicinities thereof of the particles is high and percentage of water content of the particles is low due to evaporation of water in the course of cross-linking with heating. As a result, in a case where the water absorbent resin particles are used, namely, in a case of mechanical powder transportation by a screw conveyer, a spring conveyer or the like, of powder transportation by air pressure, of powder diffusion or supply by a screw feeder or the like, of spray diffusion by air pressure, or the like, there is a problem that: the water absorbent resin particles break because of collision between the particles, collision of the particles against side walls of machines or equipments, or mechanical friction and accordingly particle size distribution changes. Further, there is a problem that: breakage of the particles decreases the effect of surface-cross-linking, or breakage of the particles produces fine particles which are the cause of dusts.

Further, there is a problem that: as the number of the fine particles increase, absorbent characteristics or gel properties drop. Therefore, in the all cases where a large amount of the water absorbent resin particles is used, solutions of these problems are desired.

[MEANS TO SOLVE THE PROBLEMS]

The inventors diligently studied so as to solve the problem. As a result of the diligent study, they found that: water is added to water absorbent resin particles after the particles are surface-cross-linked with heating and a percentage of water content is adjusted so as to be within a specific range, thereby obtaining particles having higher fracture stress, lower fragility, and more unbreakable by mechanical shear stress. As a result, the inventors completed the present invention.

Namely, a method according to the present invention is a method for producing water absorbent resin particles whose fragility is reformed, the method comprising the step of adding water to water absorbent resin particles whose main composition is acrylic acid and/or acrylic acid salt and whose surface and vicinity thereof are cross-linked with heating by a cross-linking agent having more than two functional groups capable of reacting with the acrylic acid and/or the acrylic acid salt so that water content ranges from 3 through 9%, the step being performed after the cross-linking. Further, water

absorbent resin particles according to the present invention is water absorbent resin particles whose fragility is reformed so that fracture stress of the particles is not less than 30N/m^2 , the water absorbent resin particles being obtained by adding water to absorbent resin particles whose main composition is acrylic acid and/or acrylic acid salt and whose surface and vicinity thereof are cross-linked with heating by a cross-linking agent having more than two functional groups capable of reacting with the acrylic acid and/or the acrylic acid salt so that water content ranges from 3 through 9%.

[EMBODIMENTS OF THE INVENTION]

Water absorbent resin particles according to the present invention are substantially water-insoluble resin (water absorbent resin) particles which absorb a large amount of water and swell when the particles are in contact with water so as to form hydrous gelatinized matter (hydrogel), and are water absorbent resin particles in which surfaces and vicinities thereof of the particles are cross-linked with heating by a cross-linking agent having not less than two functional groups capable of reacting with acrylic acid and/or acrylic acid salt. Such surface-cross-linked water absorbent resin is not particularly limited. Examples of the water absorbent resin include: partially neutralized cross-linked polyacrylic acid whose surface is cross-linked; partially

neutralized self-cross-linked polyacrylic acid whose surface is cross-linked; cross-linked starch-acrylic acid salt graft copolymer whose surface is cross-linked; hydrolyzed cross-linked starch-acrylonitrile graft copolymer whose surface is cross-linked, vinyl alcohol-acrylic acid salt copolymer whose surface is cross-linked, hydrolyzed cross-linked acrylic acid salt-acrylamide copolymer whose surface is cross-linked or hydrolyzed acrylic acid salt-acrylonitrile copolymer whose surface is cross-linked; and cross-linked copolymer of surface-cross-linked acrylic acid salt and 2-acrylamide-2-methylpropanesulfonic acid salt; and the like. Note that examples of salt as described above include sodium salt, potassium salt, ammonium salt, amine salt and the like. In consideration of water-absorbent characteristics of finally obtained water absorbent resin, the preferable example is cross-linked polymer of ethylene unsaturated monomer whose main component is acrylic acid and/or acrylic acid salt, and are substantially water-insoluble water-absorbent resin particles whose surface is cross-linked with heating. Note that the scope of the present invention does not include water absorbent resin particles whose surface is cross-linked without heating by using a cross-linking agent (such as polyvalent metal salt) capable of reacting with acrylic acid and/or acrylic acid salt at room temperature.

The shape of the water absorbent resin particles is not particularly limited. Examples of the shape include a scale-shape, a block-shape, a rock-shape, a pearl-shape, and an amorphous-shape, and granulated materials thereof according to the difference in a production method. However, each of the examples is applicable. In consideration of realizing eminent effects of the present invention, preferable examples include the scale-shape, the block-shape, the rock-shape, and the amorphous-shape. Further, particle size or particle size distribution is not particularly limited. Generally, the particle size ranges from approximately 10 through 1000 micron, preferably from approximately 100 through 850 micron. The particle size distribution is not less than 90 wt%. The average particle size ranges from 200 through 700 micron.

In the present invention, a cross-linking agent used to cross-link surfaces and vicinities thereof of the water absorbent resin particles is a cross-linking agent having not less than two functional groups capable of reacting with acrylic acid and/or acrylic acid salt. For example, polyglycidyl ether compound, polyvalent alcohol compound, polyamine compound, or polyamine resin. Generally, in order to cause these cross-linking agents to cross-link acrylic acid and/or acrylic acid salt of the water absorbent resin particles, heating is necessary.

Examples of polyglycidyl ether compound include ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, glycerin-1.3-diglycidyl ether, glycerin triglycidyl ether, polyethylene glycol diglycidyl ether, 1.6-hexane diol diglycidyl ether, and polyglycerol polyglycidyl ether. Examples of polyvalent alcohol compound include glycerin, ethylene glycol, diethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, diethanolamine, and triethanolamine. Examples of polyamine compound or polyamine resin include: ethylene diamine; diethylene triamine; triethylene tetramine; tetraethylene pentamine; polyamide resin which is a compound of polyamine and fatty acid; polyamine epichlorohydrin resin, and polyamide polyamine epichlorohydrin resin. Preferable examples of the surface-cross-linking agent out of the above examples include a polyglycidylether compound; a polyvalent alcohol compound; and a polyamine compound. Further preferable examples include: ethyleneglycol diglycidyl ether; propyleneglycol diglycidyl ether; glycerin triglycidyl ether; glycerin; ethyleneglycol; diethyleneglycol; and polyamide polyamine epichlorohydrin resin.

In the present invention, an amount of the surface-cross-linking agent to be used varies according to the kind of the cross-linking agent, the kind of water absorbent resin and degree of cross-linking thereof, performance target of restored water absorbent resin thus

obtained, and the like. Weight ratio of the water absorbent resin: cross-linking agent ranges from generally 100 : 0.01 through 5, preferably 100 : 0.02 through 2, more preferably 100 : 0.05 through 1. When the ratio of the cross-linking agent is less than 0.01, the effect of surface-cross-linking is not realized sufficiently. On the other hand, when the ratio is more than 5, density of surface-cross-linking increases too much, with a result that an amount of absorption drops.

In the present invention, the method for surface-cross-linking is not particularly limited and a conventional method is applicable as the method. Examples of the method include: a method in which a cross-linking agent is dissolved in a compound medium of an organic solvent and water, mixed with water absorbent resin particles, and cross-linked with heating; a method in which a cross-linking agent is dissolved in a water solution of a water-soluble compound, mixed with water absorbent resin particles, and cross-linked with heating; a method in which a water solution of a cross-linking agent is added to water absorbent resin particles in a high rate stirring state and cross-linked with heating. Note that mixture of a cross-linking agent solution and cross-linking with heating can be carried out in a single device at the same time. The present invention may be arranged so that the water absorbent resin particles are

cooled down after the cross-linking with heating. In any of the methods, it is general that water is necessary as a place for surface-cross-linking reaction.

Conditions under which cross-linking with heating is performed are not particularly limited. However, in order to carry out an effective cross-linking reaction, temperature should range generally from 100 through 200°C, preferably from 120 through 180°C. Heating time should range generally from 5 through 120 minutes, preferably from 10 through 90 minutes. In general, percentage of water content of water absorbent resin particles whose surfaces have been cross-linked under such heating conditions is not more than 2% because of evaporation of a reaction solution. Under some heating cross-linking conditions, percentage of water content is not more than 1%.

In the present invention, an amount of water to be added to the water absorbent resin particles after cross-linking with heating is not particularly limited as long as percentage of water content of the finally obtained water absorbent resin particles ranges from 3 through 9%. It is general that an amount of water ranges from 2 through 15 wt% with respect to weight of the water absorbent resin particles, it is preferable that the amount of water ranges from 2 through 12 wt%, and it is more preferable that the amount of water ranges from 3 through

9 wt%. When the amount of water to be added is less than 2 wt%, fracture stress of the particles is hardly improved. Further, when temperature of the water absorbent resin particles after the cross-linking with heating is high, a large amount of the water having been added evaporates, with a result that the effect of the present invention cannot be realized. On the other hand, when water whose amount is not less than 15 wt% is added, fracture stress of the particles is not so improved that the improvement corresponds to addition of the water. Further, adding a large amount of water causes another problem that: a block-shape object may occur due to blocking between particles and accordingly particles having even percentage of water content cannot be obtained. Here, the amount of the water to be added is larger than an amount indicative of intended water content because: when water is added under a condition that temperature of water absorbent resin particles after cross-linking with heating is high, part of added water evaporates, and accordingly it is necessary to add more water so as to cover an amount to be evaporated. Therefore, when the water absorbent resin particles are cooled down after surface-cross-linking with heating, an amount of water to be added may be smaller than the case where the water absorbent resin particles are not cooled down.

In order to prevent blocking of the particles in

adding water to the water absorbent resin particles, inorganic salt and/or inorganic hydroxide may be dissolved in water and added to the water absorbent resin particles. Examples of the inorganic salt include at least one kind selected from alkali metal salt, alkali earth metal salt, and aluminum salt. Examples of the inorganic hydroxide include aluminum hydroxide and magnesium hydroxide.

Examples of the inorganic alkali metal salt include sodium chloride, sodium sulfate, sodium carbonate, sodium phosphate, sodium alum, potassium chloride, potassium sulfate, potassium carbonate, potassium phosphate, and potassium alum. Examples of the inorganic alkaline earth metal salt include calcium chloride, magnesium chloride, and magnesium sulfate. Examples of the inorganic aluminum salt include aluminum chloride and aluminum sulfate. Preferable inorganic salt is inorganic alkaline metal salt. Further preferable inorganic salt is sodium sulfate, sodium carbonate, sodium phosphate, and sodium alum.

Density of the organic salt relative to water may vary according to the kind of the inorganic salt or to the amount of the water to be added. Generally, the density ranges from 5 through 50 wt%, preferably, the density ranges from 10 through 40 wt%. In a case where the density is less than 5 wt%, normal mixture hardly

prevents blocking in adding water. On the other hand, in a case where the density is more than 50 wt%, prevention of blocking does not increase prominently while absorption ability decreases. Therefore, the case is not preferable.

In the present invention, it is preferable that addition of water to the water absorbent resin particles is performed in a stirring mixer provided with a stirring rotor. An example is such that: while water absorbent resin particles in the stirring mixer are stirred, water (alternatively, a water solution of inorganic salt) is sprayed or dropped. In the spray or drop, a predetermined amount of water may be added at once or partially.

The stirring mixer provided with a stirring rotor may be a general mixer. Examples of the mixer include a screw-type mixer, a screw-type extruder, a turbulizer, a nauta mixer, a ribbon-type mixer, a double-armed kneader, and a double-armed multipurpose mixer. Note that the shape and the number (single or plural) of stirring rotor(s) are not particularly limited. It is general that the water absorbent resin particles obtained through adding water as described above are made into products without dry operation after the above operation. However, adjustment of percentage of water content or adjustment of particle size may be performed according to necessity.

The water absorbent resin particles according to the present invention may be arranged so that: at any stage

from the surface-cross-linking stage to the product making stage, antiseptic, fungicide, bactericide, an oxidation inhibitor, a reduction inhibitor, a perfumery, a deodorant, inorganic fine powder (such as fine silica powder), anti-moisture-absorbent blocking inhibitor and the like are added. An amount thereof to be added is generally not more than 5 wt%.

It is possible to control fracture stress of the water absorbent resin particles of the present invention through adjustment of water content by adding water. Percentage of water content of the resin particles ranges generally from 3 through 9%, preferably from 3 through 7%. Fracture stress of the particles measured by the later-mentioned method is generally not less than 30N/m^2 , preferably 30 through 100N/m^2 . In a case where water content is less than 3%, fracture stress of the particles is low, and accordingly fragility and breakability of the particles are not improved sufficiently. On the other hand, in a case where the water content is more than 9%, the particles are likely to aggregate under a condition that pressure is applied while storage or shipment. Therefore, it is not preferable. Further, in a case where the fracture stress of the particles is less than 30N/m^2 , mechanical strength of the particles is insufficient and the particles are fragile and breakable. As a result, in a case where the water absorbent resin particles are used, namely, in a

case of mechanical powder transportation by a screw conveyer, a spring conveyer or the like, of powder transportation by air pressure, of powder diffusion or supply by a screw feeder or the like, of spray diffusion by air pressure, or the like, there is a problem that: the water absorbent resin particles break due to collision between the particles, collision of the particles against side walls of machines or equipments, or mechanical friction and accordingly particle size distribution changes. Further, there is a problem that: breakage of the particles decreases the effect of surface-cross-linking so that absorbent ability or gel properties drops, or breakage of the particles produces fine particles which are the cause of dusts.

[EXAMPLES]

The following further explains the present invention with reference to examples and comparative examples. Note that the present invention is not limited to these examples and comparative examples. Water content, fracture stress of the particles, fine particle content, dust concentration, and absorbency against pressure were measured by the following method. Breakability of the particles was measured by the following method. In the following explanation, % means wt% unless particularly defined.

Water content: a sample of 5g was placed in a beaker

of 100ml and made even so as to be flat, and then placed in a non-circulating oven whose temperature was adjusted to be at 105°C. The sample was dried for two hours and cooled down to a room temperature, and then an amount having been reduced was measured. A ratio of the amount having been reduced relative to an amount of the sample before drying was regarded as water content (%).

Fracture stress of particles: a sample whose particle size ranges from 400 through 500 μ is compressed by using a creep meter (Sanden, Ltd.), and a value of stress at a time when the particles broke was obtained. The value was regarded as fracture stress (N/cm²).

Measurement of breakability of particles: a sample of 100g was placed in a ballmill (having 5 poles) and rotated for 15 minutes at a rate of 150rpm.

Fine particle content: there was provided a rotating and tapping type test equipment (Iida Manufacturing Company, Ltd.) having a JIS sieve of 140 mesh (opening is 105 μ : diameter was 20cm) and a tray. A sample of 50g was put on the sieve of 140 mesh and vibrated for 5 minutes (number of vibration: 165 time/minute). A ratio of weight of particles having passed through the 140 mesh relative to weight of the whole sample was regarded as fine particle content (%).

Dust concentration: a suction port of a suction bottle of one liter was connected with an inlet port of a digital

dust meter (Shibata Scientific Technology Ltd.) via a glass tube whose internal diameter was 7mm and whose length is 10cm. Water absorbent resin of 20g was dropped from an upper port of the suction bottle to the suction bottle via a funnel. The number of dusts produced for 1 minute included in the dropped water absorbent resin powder was measured by the digital dust meter and thus obtained value was regarded as dust concentration (CPM).

Absorbency against pressure: water absorbent resin of 0.1g was placed in a circular plastic tube (inner diameter is 30mm, height is 60mm) to a bottom face of which nylon net having 250 mesh was attached, and made even so as to be flat. A balance whose external diameter was 30mm was placed on the resin so as to be a load of 20g/cm². The plastic tube having the water absorbent resin therein was immersed and left in a plate (whose diameter is 12cm) containing physiological saline of 60ml so that the nylon net of the plastic tube faced downward. An increment in the water absorbent resin having absorbed the physiological saline was measured after 60 minutes. Thus measured value was increased by 10-fold so as to be regarded as absorbency against pressure (g/g) relative to the physiological saline.

Production Example 1

Acrylic acid of 200g, methylenebisacrylamide of 0.3g as a cross-linking agent, and ion exchanged water of 600g

were mixed so as to obtain a polymerized monomer solution and thus obtained solution was placed in a polymerizing tank capable of adiabatic polymerization. Nitrogen gas was introduced in the solution so that an amount of dissolved oxygen in the solution was not more than 0.1 ppm and a temperature of the solution was 5°C. 35% hydrogen peroxide solution of 0.03g, ascorbic acid of 0.005g, and V-50 (azo catalyst produced by Wako Pure Chemical Industries, Ltd.) of 0.1g were added to the solution. After 10 minutes, an increase in temperature indicative of the beginning of polymerization was confirmed and the temperature reached the maximum reachable temperature. The solution was further left for 4 hours, so that a gelatinized polymer was obtained. The gelatinized polymer of 600g was crushed by a small kneader so as to be small pieces, 50% NaOH water solution of 120g was added to the small pieces, and the small pieces were mixed evenly. The neutralized gel was dried by heated air and pulverized so that the particle size corresponded 20 through 145 mesh, thereby obtaining water absorbent resin particles (a). Etyleneglycol diglycidyl ether (product name: Nagase Chemicals Ltd, "DENACOL EX-810") of 0.6g had been dissolved beforehand in a mixture solution of water of 25g and methanol of 10g so as to obtain a surface-cross-linking agent solution. The water absorbent resin particles (a) of

60g was placed in a home juicer mixer whose capacity was two litter and, while stirring the water absorbent resin particles (a) at high velocity, the surface-cross-linking agent solution of 3.5g was added to the water absorbent resin particles (a) and mixed for 10 minutes. Thus obtained mixture was cross-linked with heating for 60 minutes by a hot air dryer having been adjusted so that the air was at 140°C, thereby obtaining surface-cross-linking water absorbent resin particles (a1). The water content of the (a1) was 0.8%.

Production Example 2

Polyamide polyamine epichlorohydrin resin of 1.5g had been dissolved beforehand in a mixture solution of water of 10g and methyltriglycol of 5g so as to obtain a surface-cross-linking agent. While stirring the water absorbent resin particles (a) of 120g at high velocity, the surface-cross-linking agent solution of 3g was added to the water absorbent resin particles (a) and mixed for 10 minutes. Thus obtained mixture was heated for 45 minutes by a heated air dryer having been set so that the air was 130°C, thereby obtaining surface-cross-linking water absorbent resin particles (a2). The water content of the (a2) was 1.2%.

Example 1

The water absorbent resin particles (a1) of 100g were placed in a home juicer mixer whose capacity was two

litter and, while string the water absorbent resin particles (a1) at high velocity, tap water of 4g was added and mixed for 10 minutes so as to obtain water absorbent resin particles (A) according to the present invention. An aggregate was not produced in mixture. Water content of the water absorbent resin particles (A) was 4.4%. Table 1 illustrates results of measurements of fracture stress of particles, fine particle content before measurement of breakability, dust concentration before measurement of breakability, and absorbency against pressure before measurement of breakability. Table 2 illustrates results of measurements of fine particle content after measurement of breakability, dust concentration after measurement of breakability, and absorbency against pressure after measurement of breakability.

Example 2

The water absorbent resin particles (a1) of 100g were placed in a home juicer mixer whose capacity was two litter and, while string the water absorbent resin particles (a1) at high velocity, a 20 % sodium alum solution of 6g was added and mixed for 10 minutes so as to obtain water absorbent resin particles (B) according to the present invention. An aggregate was not produced in mixture. Water content of the water absorbent resin particles (B) was 5.2%. Table 1 illustrates results of measurements of fracture stress of particles, fine particle content before

measurement of breakability, dust concentration before measurement of breakability, and absorbency against pressure before measurement of breakability. Table 2 illustrates results of measurements of fine particle content after measurement of breakability, dust concentration after measurement of breakability, and absorbency against pressure after measurement of breakability.

Example 3

Water absorbent resin particles (C) according to the present invention were obtained in the same manner as the example 2 except that an amount of the 20 % sodium alum solution to be added was reduced to 3.5g. An aggregate was not produced in mixture. Water content of the water absorbent resin particles (C) was 3.3%. Table 1 illustrates results of measurements of fracture stress of particles, fine particle content before measurement of breakability, dust concentration before measurement of breakability, and absorbency against pressure before measurement of breakability. Table 2 illustrates results of measurements of fine particle content after measurement of breakability, dust concentration after measurement of breakability, and absorbency against pressure after measurement of breakability.

Example 4

Water absorbent resin particles (D) according to the

present invention were obtained in the same manner as the example 2 except that the 20 % sodium alum solution of 6g to be added was replaced with 20 % sodium sulfate of 6g. An aggregate was not produced in mixture. Water content of the water absorbent resin particles (D) was 5.3%. Table 1 illustrates results of measurements of fracture stress of particles, fine particle content before measurement of breakability, dust concentration before measurement of breakability, and absorbency against pressure before measurement of breakability. Table 2 illustrates results of measurements of fine particle content after measurement of breakability, dust concentration after measurement of breakability, and absorbency against pressure after measurement of breakability.

Example 5

Water absorbent resin particles (E) according to the present invention were obtained in the same manner as the example 2 except that the water absorbent resin particles (a1) in the example 2 were replaced with the water absorbent resin particles (a2). An aggregate was not produced in mixture. Water content of the water absorbent resin particles (E) was 5.6%. Table 1 illustrates results of measurements of fracture stress of particles, fine particle content before measurement of breakability, dust concentration before measurement of breakability, and

absorbency against pressure before measurement of breakability. Table 2 illustrates results of measurements of fine particle content after measurement of breakability, dust concentration after measurement of breakability, and absorbency against pressure after measurement of breakability.

Comparative Examples 1 and 2

In comparison with the water absorbent resin particles (a1) and (a2), Table 1 illustrates results of measurements of fracture stress of particles, fine particle content before measurement of breakability, dust concentration before measurement of breakability, and absorbency against pressure before measurement of breakability. Table 2 illustrates results of measurements of fine particle content after measurement of breakability, dust concentration after measurement of breakability, and absorbency against pressure after measurement of breakability.

Comparative Example 3

The water absorbent resin particles (a) of 60g obtained in the production example 1 were placed in a home juicer mixer whose capacity was two litter and, while string the water absorbent resin particles (a) at high velocity, a cross-linking agent solution of 3.5g, having been obtained by dissolving ethyleneglycol diglycidil ether of 0.6g in a mixture solution of water of 25g and methanol

of 10g, was added and mixed for 10 minutes. Thus obtained mixture was heated for 60 minutes by a heated air dryer having been set so that the air was at 100°C, thereby obtaining surface-cross-linking water absorbent resin particles (a3) used for comparison. Water content of the water absorbent resin particles (a3) was 1.9%. Table 1 illustrates results of measurements of fracture stress of particles, fine particle content before measurement of breakability, dust concentration before measurement of breakability, and absorbency against pressure before measurement of breakability. Table 2 illustrates results of measurements of fine particle content after measurement of breakability, dust concentration after measurement of breakability, and absorbency against pressure after measurement of breakability.

Table 1

(Abilities before measurement of breakability)

	water content(%)	fracture stress of particles (N/m ²)	fine particle content(%)	dust concentration (cpm)	absorbency against pressure (g/g)
Example 1	4.4	61	0.6	8	34
Example 2	5.2	68	0.3	5	34
Example 3	3.3	53	0.5	9	35
Example 4	5.3	70	0.4	6	34

Example 5	5.6	73	0.4	4	33
Comparative Example 1	0.8	19	0.5	15	36
Comparative Example 2	1.2	22	0.6	17	35
Comparative Example 3	1.9	25	0.5	18	35

Table 2

(Abilities after measurement of breakability)

	fine particle content (%)	dust concentration(cpm)	absorbency against pressure (g/g)
Example 1	0.9	13	34
Example 2	0.7	11	34
Example 3	1.1	14	35
Example 4	0.8	13	34
Example 5	0.9	11	33
Comparative Example 1	4.7	82	28
Comparative Example 2	4.4	78	27
Comparative Example 3	4.1	71	28

The results of Tables 1 and 2 show that: the water

absorbent resin particles (A) through (E) according to the present invention obtained in Examples 1 through 5 are greatly improved in comparison with the water absorbent resin particles (a1) through (a3) in that: the formers have larger fracture stress of the particles than the latters, have smaller increases in fine particle content and dust concentration after measurement of breakability than the latters, and have no decrease in absorbency against pressure.

[EFFECTS OF THE PRESENT INVENTION]

With the method according to the present invention and the water absorbent resin particles according to the present invention obtained by the method according to the present invention, the following effects can be obtained.

1. The method according to the present invention allows for improvement of powder properties of water absorbent resin particles (fracture stress of particles) by an easy operation in which water is added to the water absorbent resin particles after surface-cross-linking with heating.

2. Because the fracture stress of the particles is increased, it is possible to produce water absorbent resin particles whose breakability and fragility against mechanical shear stress are improved.

3. As a result, in a case where the water absorbent resin particles are used, namely, in a case of mechanical

powder transportation by a screw conveyer, a spring conveyer or the like, of powder transportation by air pressure, of powder diffusion or supply by a screw feeder or the like, of spray diffusion by air pressure, or the like, there is little change in particle size distribution caused by collision of the particles with one another, collision of the particles with side walls of machines or equipments, or mechanical friction.

4. Even when mechanical shear stress is applied, production of fine particles caused by breakage of the particles is little and production of dusts is rare. Therefore, there is no possibility that working environment worsens or a worker absorbs dusts, so that it is safe for the worker.

5. Further, there is no decrease in absorbent ability or gel properties derived from impairment of the effect of surface-cross-linking caused by breakage of the particles.

6. In consideration of the foregoing conditions, the present invention is particularly useful in producing disposable diaper by a drum forming method. The present invention reduces clogging of the water absorbent resin particles in a screen mesh or a punching plate used to laminate pulp/absorbency resin particles.

With the foregoing effects, the water absorbent resin particles according to the present invention obtained by the method according to the present invention are useful

in all cases where transportation, supply, and diffusion of the water absorbent resin particles are carried out, and particularly useful to produce water absorbent materials, sanitary materials (such as disposable diapers for children and adults, sanitary napkins, and incontinence pads) and the like using large amount of the water absorbent resin particles. With the water absorbent resin particles according to the present invention, a product with high ability can be obtained.

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(54) 【発明の名称】 改質された吸水性樹脂粒子およびその製法

(57) 【要約】

【課題】 機械的剪断力が加わった場合の粒子の壊れ性（破断応力）および粒子脆さが改善された吸水性樹脂粒子を得る。

【解決手段】 アクリル酸および／またはアクリル酸塩を主構成単位とし、且つ該アクリル酸および／またはアクリル酸塩と反応しうる官能基を2個以上有する架橋剤で粒子表面近傍が加熱架橋された吸水性樹脂粒子に、加熱架橋後に水を添加して含水率を3～9%に調整し、粒子の破断応力を30N/m²以上とする。

【特許請求の範囲】

【請求項1】 アクリル酸および／またはアクリル酸塩を主構成単位とし、且つ該アクリル酸および／またはアクリル酸塩と反応しうる官能基を2個以上有する架橋剤で粒子表面近傍が加熱架橋された吸水性樹脂粒子に、加熱架橋後に水を添加して含水率を3～9%に調整することを特徴とする粒子脆さの改質された吸水性樹脂粒子の製法。

【請求項2】 添加する水の量が該吸水性樹脂粒子の重量に対して2～15重量%である請求項1記載の方法。

【請求項3】 添加する水が無機の塩および／または無機の水酸化物を溶解している請求項1または2記載の製法。

【請求項4】 該無機の塩が、アルカリ金属塩、アルカリ土類金属塩、アルミニウム塩から選ばれる少なくとも1種である請求項3記載の製法。

【請求項5】 該無機の塩の水に対する濃度が5～50重量%である請求項3または4に記載の方法。

【請求項6】 該吸水性樹脂粒子への水の添加を攪拌羽根を備えた攪拌混合装置内でおこなう請求項1～5のいずれかに記載の製法。

【請求項7】 該改質された吸水性樹脂粒子の破断応力が 3.0 N/m^2 以上である請求項1～6のいずれかに記載の製法。

【請求項8】 アクリル酸および／またはアクリル酸塩を主構成単位とし、且つ該アクリル酸および／またはアクリル酸塩と反応しうる官能基を2個以上有する架橋剤で粒子表面近傍が加熱架橋された吸水性樹脂粒子に水を添加して得られる、含水率が3～9%であり、粒子の破断応力が 3.0 N/m^2 以上である粒子脆さの改質された吸水性樹脂粒子。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、改質された吸水性樹脂粒子およびその製法に関する。更に詳しくは、吸水性樹脂粒子を加熱表面架橋した後に水を添加して含水率を特定範囲に調節することにより、機械的作用が加わった場合の粒子の壊れ性（破断応力）および粒子脆さを改質した吸水性樹脂粒子およびその製法に関する。

【0002】

【従来の技術】従来から、生理用品、紙おむつなどの衛生材料用途に吸水性樹脂が幅広く用いられている。このような吸水性樹脂としては、例えば、ポリアクリル酸塩架橋物、自己架橋型ポリアクリル酸塩、デンプン-アクリル酸塩グラフト共重合体架橋物などの、実質的に水不溶性の架橋重合体が知られている。近年、これら吸水性樹脂の吸収特性およびゲル物性を改良する目的で、吸水性樹脂粒子の表面近傍をアクリル酸および／またはアクリル酸塩と反応しうる官能基を2個以上有する架橋剤で加熱架橋された、いわゆる表面架橋型の吸水性樹脂が登場

している。

【0003】

【発明が解決しようとする課題】しかし、これらの加熱架橋された表面架橋型の吸水性樹脂は、従来の非加熱表面架橋型吸水性樹脂に比べて、優れた吸収特性とゲル物性を発現するが、粒子表面近傍の架橋密度が高いこと、および加熱架橋操作の過程で水分が蒸散して粒子の含水率が低いことから、樹脂粒子は硬く、且つ脆くなる。その結果、吸水性樹脂粒子を使用する場面、例えばスクリーコンベアーやスプリングコンベアー等による機械的な粉体輸送あるいは空気圧による粉体輸送、スクリーフィーダー等による粉体散布や供給、空気圧によるスプレー散布などの過程において、粒子同士の衝突、機械や設備の壁面への粒子の衝突、機械的摩擦などによって吸水性樹脂粒子が壊れて粒度分布が変化するという問題を生じる。更に、粒子が壊れることによって表面架橋の効果も損なう、粒子が壊れて微粒子が生成して粉塵の原因となるという問題も生じる。また、微粒子が増加することにより、吸収性能やゲル物性が悪化するという問題が発生する。従って、吸水性樹脂粒子を多量に使用するあらゆる場面において、これらの問題の解決が望まれている。

【0004】

【課題を解決するための手段】本発明者らは、上記の問題点を解決すべく鋭意検討した結果、吸水性樹脂粒子の加熱表面架橋後に水を添加して含水率を特定の範囲に調整することによって、粒子の破断応力がアップし、粒子の脆さが軽減され、機械的剪断力によっても壊れにくい粒子が得られることを見だし、本発明に到達した。

【0005】すなわち本発明は、アクリル酸および／またはアクリル酸塩を主構成単位とし、且つ該アクリル酸および／またはアクリル酸塩と反応しうる官能基を2個以上有する架橋剤で粒子表面近傍が加熱架橋された吸水性樹脂粒子に、加熱架橋後に水を添加して含水率を3～9%に調整することを特徴とする粒子脆さの改質された吸水性樹脂の製法；並びにアクリル酸および／またはアクリル酸塩を主構成単位とし、且つ該アクリル酸および／またはアクリル酸塩と反応しうる官能基を2個以上有する架橋剤で粒子表面近傍が加熱架橋された吸水性樹脂粒子に水を添加して得られる、含水率が3～9%であり、粒子の破断応力が 3.0 N/m^2 以上である粒子脆さの改質された吸水性樹脂粒子である。

【0006】

【発明の実施の形態】本発明において、吸水性樹脂粒子としては、水と接触したときに多量の水を吸収・膨潤して含水ゲル状物（ヒドロゲル）を形成する、実質的に水不溶性の樹脂（吸水性樹脂）の粒子であり、アクリル酸および／またはアクリル酸塩と反応しうる官能基を2個以上有する架橋剤で粒子表面近傍が加熱架橋されている吸水性樹脂粒子である。このような表面架橋型の吸水性

樹脂としては、特に限定はないが、例えば、表面架橋されたポリアクリル酸部分中和物の架橋体、表面架橋された自己架橋型ポリアクリル酸部分中和物、表面架橋されたデンプン／アクリル酸塩グラフト共重合体架橋物、表面架橋されたデンプン－アクリロニトリルグラフト重合体架橋物の加水分解物、表面架橋されたビニルアルコール／アクリル酸塩共重合体、表面架橋されたアクリル酸塩／アクリルアミド共重合体架橋物もしくはアクリル酸塩／アクリロニトリル共重合体架橋物の加水分解物、表面架橋されたアクリル酸塩と2－アクリルアミド－2－メチルプロパンスルホン酸塩の共重合体架橋物などの1種以上が挙げられる。尚、上記において塩としては、ナトリウム塩、カリウム塩、アンモニウム塩、アミン塩などが一般に用いられる。これらのうち好ましいものは、最終的に得られる吸水性樹脂の吸収特性を考えると、アクリル酸および／またはアクリル酸塩を主構成単位とするエチレン性不飽和単量体の架橋重合体であり、実質的に水不溶性の加熱表面架橋された吸水性樹脂粒子である。尚、アクリル酸および／またはアクリル酸塩と常温で反応しうる架橋剤（例えば多価金属塩など）を用い、加熱操作を加えることなく表面架橋された吸水性樹脂粒子は本発明の範囲には含まれない。

【0007】該吸水性樹脂粒子の形状は特に限定はなく、製法の違いにより、リン片状、塊状、岩状、パール状あるいは無定形状、およびこれら粒子の造粒物等が挙げられるが、いずれであってもよい。本発明の効果が顕著であるという点で好ましい形状は、リン片状、塊状、岩状あるいは無定形状である。また、粒径あるいは粒度分布についても特に限定はなく、通常約10～1,000ミクロン、好ましくは約100～850ミクロンの粒子が90重量%以上の粒度分布であり、且つ平均粒径が200～700ミクロンの粒子である。

【0008】本発明において、吸水性樹脂粒子の表面近傍を架橋するのに用いられる架橋剤としては、アクリル酸および／またはアクリル酸塩と反応しうる官能基を2個以上有する架橋剤であり、例えば、ポリグリシジルエーテル系化合物、多価アルコール系化合物、ポリアミン系化合物あるいはポリアミン系樹脂などが挙げられる。これらの架橋剤を吸水性樹脂粒子のアクリル酸および／またはアクリル酸塩と架橋反応させるには加熱操作を必要とするのが通常である。

【0009】ポリグリシジルエーテル系化合物の具体例としては、エチレングリコールジグリシジルエーテル、プロピレングリコールジグリシジルエーテル、グリセリン－1,3－ジグリシジルエーテル、グリセリントリグリシジルエーテル、ポリエチレングリコールジグリシジルエーテル、1,6－ヘキサジオールジグリシジルエーテル、ポリグリセロールポリグリシジルエーテル等が挙げられる。多価アルコール系化合物の具体例としては、グリセリン、エチレングリコール、ジエチレングリ

コール、プロピレングリコール、ポリエチレングリコール、ポリプロピレングリコール、ジエタノールアミン、トリエタノールアミン等が挙げられる。ポリアミン系化合物あるいはポリアミン系樹脂の具体例としては、エチレンジアミン、ジエチレントリアミン、トリエチレントラミン、テトラエチレンペンタミン、ポリアミンと脂肪酸との反応物であるポリアミド樹脂、ポリアミンエピクロルヒドリン樹脂、ポリアミドポリアミンエピクロルヒドリン樹脂等が挙げられる。該表面架橋剤として例示したもののうち好ましいものは、ポリグリシジルエーテル系化合物、多価アルコール系化合物およびポリアミン系化合物である。更に好ましいものは、エチレングリコールジグリシジルエーテル、プロピレングリコールジグリシジルエーテル、グリセリン－1,3－ジグリシジルエーテル、グリセリントリグリシジルエーテル、ポリグリセロールポリグリシジルエーテル、グリセリン、エチレングリコール、ジエチレングリコール、ポリアミドポリアミンエピクロルヒドリン樹脂である。

【0010】本発明において該表面架橋剤の使用量は、架橋剤の種類、吸水性樹脂の種類およびその架橋度、得られる改質された吸水性樹脂の性能目標などによっても異なるが、吸水性樹脂：架橋剤の重量比で、通常100:0.01～5、好ましくは100:0.02～2、特に好ましくは100:0.05～1の範囲である。この架橋剤の比率が0.01未満では表面架橋の効果が十分発現せず、反対に5より多い場合は表面架橋の密度が過大となりすぎて吸収量の低下をまねく。

【0011】本発明において、表面架橋の方法については特に限定はなく従来からの方法が適用でき、例えば、有機溶剤と水との混合溶媒に架橋剤を溶解して吸水性樹脂粒子と混合した後に加熱架橋する方法、水溶性化合物の水溶液に架橋剤を溶解して吸水性樹脂粒子と混合した後に加熱架橋する方法、高速攪拌状態の吸水性樹脂粒子に架橋剤水溶液を添加した後に加熱架橋する方法などが挙げられる。尚、架橋剤溶液の混合と加熱架橋操作とを同時に同じ装置内で行うこともできる。上記の加熱架橋後に吸水性樹脂粒子を冷却する操作を加えても良い。いずれの方法においても、表面架橋反応に当たっては、反応の場として水の存在を必要とするのが通常である。

【0012】加熱架橋の条件についても特に限定はないが、効率的な架橋反応を行わせるためには通常100～200℃、好ましくは120～180℃の温度が必要であり、加熱時間は通常5～120分、好ましくは10～90分である。このような加熱条件で表面架橋された後の吸水性樹脂粒子は、反応溶媒の蒸発により、通常含水率は2%以下となる。加熱架橋条件によっては含水率が1%以下になる場合がある。

【0013】本発明において、加熱架橋後に添加する水の量は、最終的に得られる吸水性樹脂粒子の含水率が3～9%にできれば特に限定はないが、該吸水性樹脂粒子

の重量に対して通常2~15重量%であり、好ましくは3~12重量%、更に好ましくは3~9重量%である。添加する水の量が2重量%未満の場合、粒子の破断応力を改善する効果が殆ど認められない。また、加熱架橋後の吸水性樹脂粒子の温度が高い場合には添加した水の大部分が蒸発してしまうため、本発明の効果が得られなくなる。一方、15重量%を越える水を添加しても、水の添加に見合う粒子の破断応力の改善効果が得られないことから非経済的である。更に、多量の水を添加することから粒子同士のブロッキングにより塊状物を生じやすくなり、均一な含水率を有する粒子が得られないという別の問題が発生する。ここで、添加する水の量が目的とする含水率よりも多い量であるのは、加熱架橋後の吸水性樹脂粒子の温度が高い状態で水を添加した場合、添加した水の一部が蒸発するため、この蒸発分を見込んで多めに添加する必要があるためである。従って、加熱表面架橋後に吸水性樹脂粒子を冷却する操作を加えた場合には、冷却操作を加えない場合に比べて添加する水の量は少なくてもよい。

【0014】吸水性樹脂粒子に水を添加する際に粒子同士のブロッキングを生じさせない目的で、必要により水に無機の塩および/または無機の水酸化物を溶解して添加することができる。このような無機の塩としては、アルカリ金属塩、アルカリ土類金属塩、アルミニウム塩から選ばれる少なくとも1種の無機塩が挙げられる。無機の水酸化物としては、水酸化アルミニウム、水酸化マグネシウムなどが挙げられる。

【0015】無機アルカリ金属塩の具体例としては、塩化ナトリウム、硫酸ナトリウム、炭酸ナトリウム、リン酸ナトリウム、ナトリウム明礬、塩化カリウム、硫酸カリウム、炭酸カリウム、リン酸カリウム、カリウム明礬などが挙げられる。無機アルカリ土類金属塩の具体例としては、塩化カルシウム、塩化マグネシウム、硫酸マグネシウムなどが挙げられる。無機アルミニウム塩の具体例としては、塩化アルミニウム、硫酸アルミニウムなどが挙げられる。好ましい無機塩は無機アルカリ金属塩であり、特に好ましいものは硫酸ナトリウム、炭酸ナトリウム、リン酸ナトリウム、ナトリウム明礬である。

【0016】該無機の塩の水に対する濃度は無機塩の種類や添加する水の量によって種々変化させることができるが、通常5~50重量%、好ましくは10~40重量%である。濃度が5重量%未満の場合、通常の混合では水添加時のブロッキングを防止する効果に乏しく、一方、濃度が50重量%を越えてもブロッキングを防止する効果に顕著な向上は認められず、且つ吸収性能が低下する結果を招き好ましくない。

【0017】本発明において、該吸水性樹脂粒子に水を添加する方法としては、攪拌羽根を備えた攪拌混合装置内でおこなうのが好ましい。例えば、攪拌混合装置内に供給された吸水性樹脂粒子を攪拌しながら水（または無

機塩を溶解した水）を噴霧あるいは滴下する方法が挙げられる。噴霧や滴下に当たっては、所定量の一括添加あるいは分割添加のいずれでもよい。

【0018】攪拌羽根を備えた攪拌混合装置としては、通常の混合装置でよく、例えば、スクリュウ型混合機、スクリュウ型押出機、タービュライザー、ナウター型混合機、リボン型混合機、双腕型ニーダー、双腕型万能混合機などが挙げられる。尚、攪拌羽根の形状および数（単数または複数）については特に限定はない。上記のように水を添加して得られたの吸水性樹脂粒子は、その後の乾燥操作なしに製品化されるのが通常であるが、必要により含水率調整や粒度調整操作を施してもよい。

【0019】本発明の吸水性樹脂粒子は、表面架橋後から製品化までの任意の段階で、防腐剤、防かび剤、抗菌剤、酸化防止剤、還元性防止剤、芳香剤、消臭剤、無機微粉末（シリカ微粉末など）、耐吸湿ブロッキング防止剤などを添加したものとすることができ、その添加量は通常5重量%以下である。

【0020】本発明の吸水性樹脂粒子の破断応力は、水の添加による含水率の調整によってコントロールすることができる。樹脂粒子の含水率は3~9%、好ましくは3~7%であり、後述する方法で測定される粒子の破断応力は通常30N/m²以上、好ましくは30~100N/m²である。含水率が3%未満では粒子の破断応力が低く、粒子の脆さや壊れ性の改善効果に乏しい。一方9%を越えると貯蔵中あるいは輸送中などにおける荷重が加わる条件下で粒子同士の凝集が生じやすくなり好ましくない。また、粒子の破断応力が30N/m²未満の場合、粒子の機械的強度が不十分となり、脆く壊れやすい粒子となる。その結果、吸水性樹脂粒子を使用する場合、例えばスクリュウコンベアーやスプリングコンベアー等による機械的な輸送あるいは空気圧による輸送の場合、スクリュウフィーダー等で供給・散布したり、空気圧でスプレー散布する工程において、粒子同士の衝突、機械や設備の壁面への粒子の衝突、機械的摩擦などによって吸水性樹脂粒子が壊れて粒度分布が変化するという問題を生じる。更に、粒子が壊れることによって表面架橋の効果を損なって吸収性能やゲル物性が悪化する、粒子が壊れて微粒子が生成することによって粉塵が発生するという問題が発生する。

【0021】

【実施例】以下、実施例および比較例により本発明をさらに説明するが、本発明はこれらに限定されるものではない。含水率、粒子の破断応力、微粒子含量、粉塵度および加圧吸収量は下記の方法により測定し、粒子の壊れ性試験は下記の方法で実施した。以下、特に定めない限り、%は重量%を示す。

【0022】含水率：100mlビーカーにサンプル5gを入れて平坦に均した後、105℃に調整された非循環型オーブンの中に入れる。2時間乾燥後、室温まで冷

却した後、減少した重量を測定する。この減少重量の乾燥前サンプル重量に対する比を含水率（単位％）とした。

【0023】粒子の破断応力：400～500ミクロンの粒径のサンプルをクリープメーター（山電株式会社製）を用いて圧縮試験し、粒子が破断する時の応力値を求めて破断応力（単位N/cm²）とした。

【0024】粒子の壊れ性試験：サンプル100gをボールミル（ボール数5個）に入れ、毎分150回転で15分間回転させる。

【0025】微粒子含量：140メッシュ（目開き105ミクロン；直径20cm）のJISフルイと受け皿がセットされたロータップ試験機（飯田製作所製）に、サンプル50gを140メッシュフルイの上に載せ、5分間振動させる（振動数：毎分165回）。140メッシュを通過した粒子重量の全サンプル重量に対する比を微粒子含量（単位％）とした。

【0026】粉塵度：1リットル吸引瓶の吸引口とデジタル粉塵計（柴田科学製）の吸入口を内径7mm、長さ10cmのガラス管で接続する。吸引瓶の上部の口から、ロートを用いて吸水性樹脂20gを吸引瓶に落下させる。落下させた吸水性樹脂粉末中の1分間に発生した粉塵の個数をデジタル粉塵計を用いて測定し、この値を粉塵度（単位CPM）とした。

【0027】加圧吸収量：250メッシュのナイロン網を底面に貼った円筒型プラスチックチューブ（内径30mm、高さ60mm）内に吸水性樹脂0.1gを入れて平坦に均す。この樹脂の上に20g/cm²の荷重となるように外径30mmの分銅を乗せる。生理食塩水60mlの入ったシャーレ（直径：12cm）の中に吸水性樹脂の入ったプラスチックチューブをナイロン網側を下面にして浸し、放置する。吸水性樹脂が生理食塩水を吸収して増加した重量を60分後に測定し、この10倍値を生理食塩水に対する加圧吸収量（単位g/g）とした。

【0028】製造例1

アクリル酸200g、架橋剤としてメチレンビスアクリルアミド0.3g、イオン交換水600gを混合して重合性単量体水溶液を調整し、この混合液を断熱重合可能な重合槽に投入した。溶液中に窒素ガスを導入することにより、溶液中の溶存酸素量を0.1ppm以下、溶液温度を5℃とした。この重合溶液に、35%過酸化水素水0.03g、アスコルビン酸0.005g、V-50（和光純薬工業製アゾ系触媒）0.1gを添加した。10分後に重合開始を示す温度上昇が確認され、約3時間後に最高到達温度に達した。更に4時間熟成してゲル状重合体を得た。このゲル状重合体600gを小型ニーダーを用いて小片に碎断した後、これに50%のNaOH水溶液120gを添加し、均一に混合した。この中和されたゲルを熱風乾燥した後、20～145メッシュの

粒度に粉碎して吸水性樹脂粒子（a）を得た。あらかじめエチレングリコールジグリシジルエーテル（製品名：ナガセ化成工業（株）「デナコールEX-810」）

0.6gを、水25gとメタノール10gの混合液に溶解して表面架橋剤溶液を作成した。吸水性樹脂粒子

（a）60gを容量2リットルの家庭用ジュサーミキサーに入れ、高速攪拌しながら上記表面架橋剤溶液3.5gを添加して十分混合した。この混合物を、140℃に調整した熱風乾燥機で60分間加熱架橋し、表面架橋型吸水性樹脂粒子（a1）を得た。（a1）の含水率は0.8%であった。

【0029】製造例2

あらかじめポリアミドポリアミンエピクロルヒドリン樹脂1.5gを、水10gとメチルトリグリコール5gの混合液に溶解して表面架橋剤溶液を作成した。吸水性樹脂粒子（a）120gを高速攪拌しながら上記表面架橋剤溶液3gを添加して十分混合した。この混合物を、130℃に調整した熱風乾燥機で45分間加熱し、表面架橋型吸水性樹脂粒子（a2）を得た。（a2）の含水率は1.2%であった。

【0030】実施例1

吸水性樹脂粒子（a1）100gを容量2リットルの家庭用ジュサーミキサーに入れ、高速攪拌しながら水道水4gを添加して十分混合することにより本発明の吸水性樹脂粒子（イ）を得た。混合中に凝集塊の生成は見られなかった。得られた吸水性樹脂粒子（イ）の含水率は4.4%であった。粒子の破断応力、および壊れ性試験前の微粒子含量、粉塵度、加圧吸収量の測定結果を表1に、壊れ性試験後の微粒子含量、粉塵度、加圧吸収量の測定結果を表2に示す。

【0031】実施例2

吸水性樹脂粒子（a1）100gを容量2リットルの家庭用ジュサーミキサーに入れ、高速攪拌しながらナトリウム明礬20%水溶液6gを添加して十分混合することにより本発明の吸水性樹脂粒子（ロ）を得た。混合中に凝集塊の生成は見られなかった。得られた吸水性樹脂粒子（ロ）の含水率は5.2%であった。粒子の破断応力および壊れ性試験前の微粒子含量、粉塵度、加圧吸収量の測定結果を表1に、壊れ性試験後の微粒子含量、粉塵度、加圧吸収量の測定結果を表2に示す。

【0032】実施例3

実施例2において、ナトリウム明礬20%水溶液の添加量を3.5gとする以外は実施例2と同様にして本発明の吸水性樹脂粒子（ハ）を得た。混合中に凝集塊の生成は見られなかった。得られた吸水性樹脂粒子（ハ）の含水率は3.3%であった。粒子の破断応力および壊れ性試験前の微粒子含量、粉塵度、加圧吸収量の測定結果を表1に、壊れ性試験後の微粒子含量、粉塵度、加圧吸収量の測定結果を表2に示す。

【0033】実施例4

実施例 2 において、ナトリウム明礬 20% 水溶液 6 g に代えて、硫酸ナトリウム 20% 水溶液を同量使用する以外は実施例 2 と同様にして本発明の吸水性樹脂粒子

(二) を得た。混合中に凝集塊の生成は見られなかった。得られた吸水性樹脂粒子 (二) の含水率は 5.3% であった。粒子の破断応力および壊れ性試験前の微粒子含量、粉塵度、加圧吸収量の測定結果を表 1 に、壊れ性試験後の微粒子含量、粉塵度、加圧吸収量の測定結果を表 2 に示す。

【0034】実施例 5

実施例 2 の吸水性樹脂粒子 (a 1) に代えて、吸水性樹脂粒子 (a 2) を使用する以外は実施例 2 と同様にして本発明の吸水性樹脂粒子 (木) を得た。混合中に凝集塊の生成は見られなかった。得られた吸水性樹脂粒子

(木) の含水率は 5.6% であった。粒子の破断応力および壊れ性試験前の微粒子含量、粉塵度、加圧吸収量の測定結果を表 1 に、壊れ性試験後の微粒子含量、粉塵度、加圧吸収量の測定結果を表 2 に示す。

【0035】比較例 1 および 2

吸水性樹脂粒子 (a 1) および (a 2) を比較の吸水性
 <壊れ性試験前の性能>

樹脂粒子とし、粒子の破断応力および壊れ性試験前の微粒子含量、粉塵度、加圧吸収量の測定結果を表 1 に、壊れ性試験後の微粒子含量、粉塵度、加圧吸収量の測定結果を表 2 に示す。

【0036】比較例 3

製造例 1 で得られた吸水性樹脂粒子 (a) 60 g を容量 2 リットルの家庭用ジュサーミキサーに入れ、高速攪拌しながら、あらかじめエチレングリコールジグリシジルエーテル 0.6 g を、水 25 g とメタノール 10 g の混合液に溶解して作成した表面架橋剤溶液 3.5 g を添加して十分混合した。この混合物を、100℃に調整した熱風乾燥機で 60 分間加熱し、比較の表面架橋型吸水性樹脂粒子 (a 3) を得た。(a 3) の含水率は 1.9% であった。粒子の破断応力および壊れ性試験前の微粒子含量、粉塵度、加圧吸収量の測定結果を表 1 に、壊れ性試験後の微粒子含量、粉塵度、加圧吸収量の測定結果を表 2 に示す。

【0037】

【表 1】

	含水率	粒子の破断応力	微粒子含量	粉塵度	加圧吸収量
	(%)	(N/m ²)	(%)	(cpm)	(g/g)
-----	-----	-----	-----	-----	-----
実施例 1	4.4	61	0.6	8	34
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実施例 2	5.2	68	0.3	5	34
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実施例 3	3.3	53	0.5	9	35
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実施例 4	5.3	70	0.4	6	34
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実施例 5	5.6	73	0.4	4	33
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比較例 1	0.8	19	0.5	15	36
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比較例 2	1.2	22	0.6	17	35
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比較例 3	1.9	25	0.5	18	35
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【0038】

【表 2】

<壊れ性試験後の性能>

	微粒子含量 (%)	粉塵度 (cpm)	加圧吸収量 (g/g)
実施例 1	0.9	13	34
実施例 2	0.7	11	34
実施例 3	1.1	14	35
実施例 4	0.8	13	34
実施例 5	0.9	11	33
比較例 1	4.7	82	28
比較例 2	4.4	78	27
比較例 3	4.1	71	28

【0039】表1および表2の結果から、実施例1～5で得られた本発明の吸水性樹脂粒子（イ）～（ホ）は、比較例1～3の比較の吸水性樹脂粒子（a1）～（a3）に比べて粒子の破断応力が大きく、壊れ性試験後においても微粒子含量の増加および粉塵度の増加が少なく、加圧吸収量の低下もないことから、飛躍的な改善が認められる。

【0040】

【発明の効果】本発明の方法、および本発明の方法により得られる本発明の吸水性樹脂粒子はは次のような効果を奏する。

①本発明の方法は、加熱表面架橋後に水を添加するという簡単な操作で吸水性樹脂粒子の粉体物性（粒子の破断応力）を改質することができる。

②粒子の破断応力がアップする結果、機械的剪断力に対する壊れ性、粒子脆さの改善された吸水性樹脂粒子が製造できる。

③その結果、吸水性樹脂粒子を使用する場面、例えばスクリュコンベアーやスプリングコンベアー等による機械的な輸送あるいは空気圧による輸送の場面、スクリュフィーダー等で供給・散布したり、空気圧でスプレー散布する工程において、粒子同士の衝突、機械や設備の壁面への粒子の衝突、機械的摩擦などによる粒度分布の変化が少ない。

④機械的剪断力が加わっても粒子の壊れによる微粒子の生成が少なく、粉塵発生がほとんどないことから、作業環境を悪化させる心配や、粉塵吸入の心配が無いことから作業者に安全である。。

⑤更に、粒子の壊れによって表面架橋の効果を損なうことによる、吸収性能やゲル物性の悪化がない。

⑥上記のことから、ドラムフォーミング方式で紙おむつを製造する場合に特に有用であり、パルプ/吸水性樹脂粒子積層用のスクリーンメッシュやパンチングプレートへの吸水性樹脂粒子の目詰まりが少なくなる。

【0041】上記効果を奏することから、本発明の方法により得られる本発明の吸水性樹脂粒子は、吸水性樹脂粒子の輸送、供給、散布を伴うあらゆる場面に有用である。特に吸水性樹脂粒子を多量に取り扱う吸収性当材、衛生材料（子供用および大人用紙おむつ、生理用ナプキン、失禁用パッド等）等の製造に有用であり、性能の優れた製品が得られる。

フロントページの続き

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